Space-charge-limited hole current in poly(9,9-dioctylfluorene) diodes

Nicolai, H. T.; Wetzelaer, G. A. H.; Kuik, M.; Kronemeijer, A. J.; de Boer, B.; Blom, P. W. M.

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Space-charge-limited hole current in poly(9,9-dioctylfluorene) diodes

H. T. Nicolai, G. A. H. Wetzelaer, M. Kuik, A. J. Kronemeijer, B. de Boer, and P. W. M. Blom[a)]

Molecular Electronics, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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Characterization of the hole transport in blue-emitting polymers as poly(9,9-dioctylfluorene) (PFO) is strongly hindered by their large ionization potential of ~6 eV. Using common anodes as poly(3,4-ethylenedioxythiophene)/poly(styrenesulphonic acid) leads to a strongly injection limited current. We demonstrate that molybdenum trioxide forms an Ohmic hole contact on PFO, enabling the observation of a space-charge-limited current(SCLC). This allows a direct determination of the hole mobility PFO of 1.3×10^{-9} m^2/V s at room temperature, in good agreement with previously reported mobility values determined by time-of-flight measurements. © *2010 American Institute of Physics*. [doi:10.1063/1.3391668]

In the past decade polymer light-emitting diodes (PLEDs) have received much attention due to their potential for easy fabrication of flexible full-color displays and lighting applications. However, an issue impeding a breakthrough in polymer devices is stability; many polymers suffer from degradation under the influence of oxygen or water. A higher electron affinity [deeper lowest unoccupied molecular orbital (LUMO) level] is beneficial for the stability.[1] However, a lowering of the LUMO of light-emitting polymers with a certain band gap would automatically imply a lowering of the highest occupied molecular orbital (HOMO) as well. This in turn will strongly reduce the injection of holes into the HOMO from standard anodes as poly(3,4-ethylenedioxythiophene)/poly(styrenesulphonic acid) (PEDOT:PSS), complicating the realization of efficient LEDs with balanced charge transport. As an example, poly(9,9-dioctylfluorene) (PFO) is an attractive material to function as the blue host material in white light-emitting PLEDs due to its efficient blue emission and high mobility.[2,3] The HOMO level of PFO is located at 5.8 eV below vacuum,[4] leading to a significant hole injection barrier of 0.6 eV when combined with PEDOT:PSS with a work function of approximately 5.2 eV.[5] Such an injection barrier will strongly hamper the hole current and limit the device performance.

It has been shown that an Ohmic hole contact can nevertheless be formed on PFO using PEDOT:PSS by electrical conditioning the PLED.[6,7] It is usually observed that the current density-voltage (*J-V*) curve of PFO PLEDs with a PEDOT:PSS anode shows a switching effect in the first scan due to trapping of electrons near the anode. These trapped electrons induce an interfacial dipole and reduce the injection barrier for hole injection. After electrical conditioning the hole contact could be even considered as Ohmic.[6] Since the formation of the Ohmic contact is driven by trapped electrons, this effect relies on the presence of an electron current. Furthermore, due to slow detrapping of the electrons the efficiency of the hole injection slowly decreases in time. Accordingly a switching effect is not observed in hole-only devices of PFO and the hole current in such a device is severely injection limited.[8] Since the current is not space-charge limited (SCL) the hole mobility cannot directly be determined from hole-only devices using PEDOT:PSS as hole injection layer (HIL). In best case, an estimate of the hole mobility can be extracted from the double carrier current. In Fig. 1 the first scan of a *J-V* curve of a PEDOT:PPS/PFO/Ba/Al PLED is shown: using a numerical drift-diffusion model[9] we calculate the current assuming Langevin recombination. For this we assume the electron mobility to be equal to the hole mobility, an assumption which is supported by measurements of Chua *et al.*[10] who reported similar mobilities for holes and electrons in field-effect transistors and by measurements from Zhang *et al.*[11] who reported identical mobilities for electrons and holes in MEH-PPV by disabling electron traps trough n-type doping. Under these assumptions the PLED current can be modeled using a low-field mobility for both electrons and holes of 2×10^{-9} m^2/V s. This value of the mobility is comparable to values obtained by time-of-flight (TOF) measurements which range from 2×10^{-9} to 3×10^{-8} m^2/V s.[3,12,13] The rather large spread of reported hole mobility values can be explained by the complex morphology of PFO.[14] It has been shown that PFO can exhibit different phases[15] and that therefore the morphology and transport properties can depend strongly on the processing conditions.

To find out if the hole transport in the PEDOT:PSS PLED after electrical conditioning is bulk limited (implying

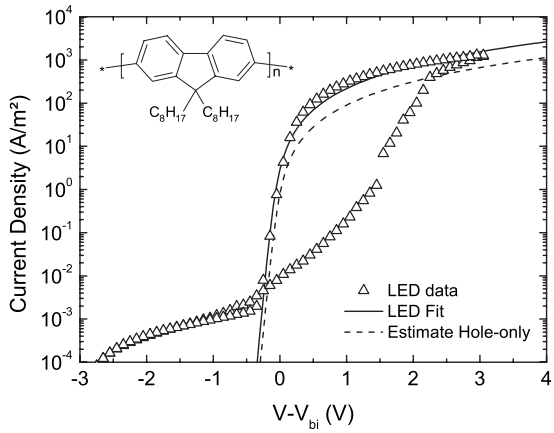

FIG. 1. *J-V* characteristics of a 100 nm PFO LED using a PEDOT:PSS HIL.

a)Electronic mail: p.w.m.blom@rug.nl.

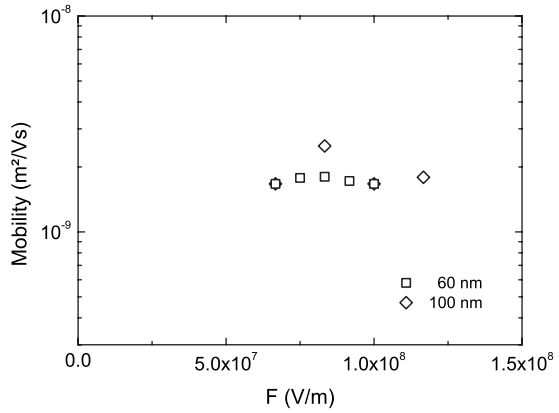

FIG. 2. The hole mobility as a function of electric field for two devices with thicknesses of 60 and 100 nm, determined with TEL.

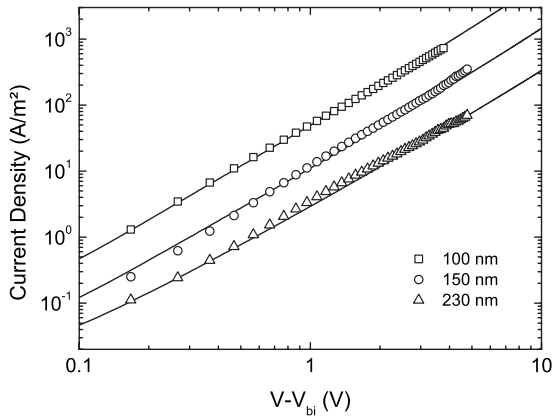

FIG. 3. *J-V* characteristics of PFO hole-only devices with a MoO_3 HIL and fits at 295 K.

Ohmic contacts), or still limited by the hole injection, we have measured the hole mobility with transient electroluminescence (TEL).[16] In this technique a voltage pulse of varying duration τ_{pulse} is applied, maintaining a constant repetition frequency. The delay time τ_d between this pulse and the resulting electroluminescence is derived from the relation between photocurrent and pulse length τ_{pulse}. This delay time τ_d is a direct measure of the transit time of the fastest carrier (holes) toward the recombination zone at the other electrode, from which the charge carrier mobility can directly be calculated. In OC1C10-PPV the observed mobility exhibited a dependence on sample thickness, which is an indication of dispersive transport.[16] From TOF experiments on PFO [8] it has been shown that the hole transport in PFO is nondispersive. As a result the TEL technique will provide direct information on the charge carrier mobility. The results for two PEDOT:PSS/PFO PLEDs with different thicknesses are shown in Fig. 2. It is observed that the mobility is indeed independent of the thickness, indicating nondispersive hole transport. From the measurements in Fig. 2 a hole mobility of $\mu_h = 2.0 \times 10^{-9}$ $m^2/V\,s$ is found, in excellent agreement with the mobility as obtained from modeling of the PLED current.

Recently transition metal oxides gained interest as hole injection layers in organic devices.[17,18] Specifically molybdenum trioxide (MoO_3) has proven to be an attractive material and has been used as a HIL in organic LEDs based on small molecules,[19–22] as buffer layer in organic solar cells[23,24] and as connecting layer in tandem organic LEDs.[25] The working mechanism of MoO_3 as HIL is generally ascribed to the formation of an interfacial dipole and consequently a reduction of the injection barrier.[26,27] More specifically, Kröger *et al.*[28] reported MoO_3 to be a n-type material with a high electron affinity (EA) of 6.7 eV. The hole injection of MoO_3 into the semiconductor was described to proceed by electron extraction from the HOMO of the semiconductor trough the conduction band of MoO_3.[29] MoO_3 has also proven to be an efficient p-type dopant,[30,31] which can be understood from the high EA.

Single carrier hole-only devices of PFO were fabricated, using MoO_3 as HIL. We note that in this case the MoO_3 layer was evaporated as top contact and that the PEDOT:PSS bottom contact functions as an electron-blocking cathode. PEDOT:PSS was spincoated on a glass substrate with a patterned indium tin oxide layer. The PFO layer was spincoated from a toluene solution. The top contact was evaporated trough a shadow mask at a base pressure of approximately 10^{-6} mbar and consisted of a 15 nm MoO_3 layer followed by a 100 nm aluminum capping layer. The MoO_3 layer thickness of 15 nm was found to be the optimal layer thickness with regards to device current and stability. *J-V* characteristics were measured in a nitrogen atmosphere using a computer controlled Keithley 2400 SourceMeter.

Figure 3 shows the *J-V* curves of three PFO hole-only devices of different thicknesses, corrected for the built-in potential V_{bi}. A clear quadratic dependence of the device current on the voltage is observed indicating a SCL current. The mobility can then be directly obtained from the *J-V* curve using Mott–Gurney's square law,

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{(V - V_{bi})}{L^3}, \tag{1}$$

where $\varepsilon_0\varepsilon_r$ is the dielectric constant, μ the mobility, V the applied voltage, and L the active layer thickness. Thus, a SCLC has now been observed in a polymer with a very deep HOMO level.

At higher voltages a deviation from Eq. (1) is observed for the thin devices due to the field and charge carrier density dependence of the mobility.[32,33] At low voltages using Eq. (1) a mobility of 1.3×10^{-9} $m^2/V\,s$ is obtained, which agrees very well with the mobility obtained from TEL and the double carrier current. This confirms that MoO_3 is indeed a truly Ohmic contact on PFO.

Equation (1) is an approximation and only valid for a constant mobility, and neglecting diffusion. For a complete description, diffusion effects from the contacts,[34] the charge carrier density dependence and field dependence of the mobility need to be taken into account. The occurrence of a SCL current enables us now to also further investigate the density- and field dependence of the hole mobility of PFO. The experimental data were therefore fitted with a numerical drift-diffusion model[9] in which the density and field dependence of the mobility are described by the following:[35]

$$\mu_p(T,p,E) \approx \mu_p(T,p)f(T,E), \tag{2}$$

$$\mu_p(T,p) = \mu_0(T)\exp\left[\frac{1}{2}(\hat{\sigma}^2 - \hat{\sigma})\left(2\frac{p}{N_t}\right)^{\delta}\right], \tag{3}$$

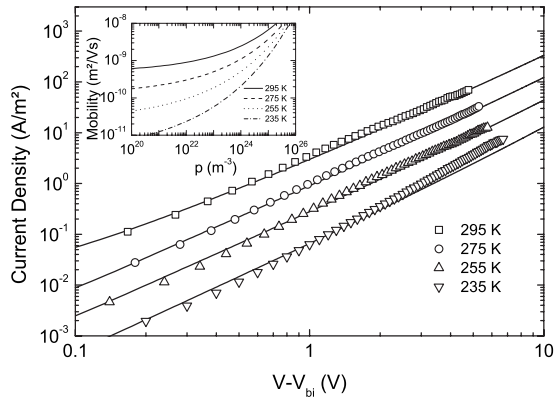

FIG. 4. Temperature dependence of a 230 nm PFO hole-only device and fits. The inset shows the dependence of the mobility on the charge carrier density according to Eqs. (2)–(5).

$$\delta = 2\frac{\ln(\hat{\sigma}^2 - \hat{\sigma}) - \ln[\ln(4)]}{\hat{\sigma}^2}, \tag{4}$$

$$f(T,E) = \exp\left[0.44(\hat{\sigma}^{3/2} - 0.22)\left\{\sqrt{1 + 0.8\left(\frac{Eea}{\sigma}\right)^2} - 1\right\}\right], \tag{5}$$

where $\mu_0(T)$ is the mobility in the limit of zero charge carrier density and electric field, $\hat{\sigma} \equiv \sigma / k_B T$ and σ is the width of the Gaussian density of states, N_t the density of transport sites and $a = N_t^{-1/3}$ the intersite distance. The thickness dependence (Fig. 3) and temperature dependence (Fig. 4) could be consistently described with a single set of parameters, $\sigma = 0.13$ eV and $N_t = 1 \times 10^{28}$ m^{-3}. The same value for σ was recently found for a polyfluorene derivative by Van Mensfoort *et al.*[36] The fact that the model gives a good description of the thickness dependence suggests that the MoO_3 does not diffuse into the active layer. In the inset of Fig. 4 the resulting dependence of the hole mobility of PFO on hole density is shown for various temperatures. As compared to poly(*p*-phenylene vinylene) derivatives the mobility starts to rise at slightly higher carrier densities of $\sim 5 \times 10^{22}$ m^{-3}.[35] However, due to the smaller σ in PFO, which is also reflected in a higher low-field mobility, the increase in the mobility with density is weaker. This also explains why in Fig. 3 the quadratic regime of the current density versus voltage plot is clearly discernible in the low voltage regime.

In conclusion, we have realized Ohmic hole injection in a PFO hole-only device using MoO_3 HIL. This enables us to measure a SCL current and to directly determine the hole mobility of PFO from *J*-*V* measurements, which is not possible using the common HIL PEDOT:PSS. The zero-field hole mobility was determined to be 1.3×10^{-9} m^2/V s, agreeing well with previously reported mobilities measured by TEL and TOF. The fact that MoO_3 can form an Ohmic contact on PFO proves its potential as HIL and opens the door to the use of polymers with deeper HOMO and LUMO levels.

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